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A Study Of The Catalytic Action Of
Colloidal Platinum On The Decomposition
Of Hydrogen Peroxide

A STUDY OF THE CATALYTIC ACTION OF
COLLOIDAL PLATINUM
ON THE
DECOMPOSITION OF HYDROGEN PEROXIDE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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A STUDY OF THE CATALYTIC ACTION OF COLLOIDAL
PLATINUM ON THE DECOMPOSITION OF HYDROGEN PEROXIDE

I. Introduction.

A large amount of research has been carried out in the study of the catalytic action of platinum. Among the most suitable substances for this investigation is hydrogen peroxide. In spite of the great amount of time and effort expended by investigators in this field, the exact mechanism of this process is not yet thoroughly understood.

There is a similarity between the catalytic action of platinum on hydrogen peroxide and the action of organic ferments, blood, etc. Indeed this resemblance is so pronounced that Bredig gives his articles the title "Über Anorganische Fermente". The resemblance is especially noticeable in the effect of certain poisons on the catalysis. Bredig* found that mere traces of such poisons as hydrocyanic acid and hydrogen sulfide caused a large decrease in the catalytic action not only of platinum but of organic ferments and of blood corpuscles. On finding that respiratory and circulatory (blood) poisons have the most marked effect, one is led to suspect a similarity between enzymes

*Z. Physik. Chem. 37, pp. 1-68. (1901).

and platinum which might be called an inorganic ferment.

Among the investigators on the catalytic action of platinum Bredig* obtained the most satisfactory results. He used in his research colloidal platinum and a hydrogen peroxide solution which was probably free from electrolytes; it contained nothing but pure hydrogen peroxide mixed with conductivity water. He showed that the velocity of the catalyzed decomposition increased decidedly with each succeeding interval of time.

The results obtained in the present research did not agree with those of Bredig's in that the velocity usually decreased to about the same degree that his increased. This lack of agreement is probably due to a difference in the methods of purifying the hydrogen peroxide solution and also in preparing the colloidal platinum. These differences will be discussed later.

One object of this research was to study the velocity of decomposition with varying concentrations of peroxide and of platinum. Comparison was also made of the velocity of decomposition of peroxide solutions which had been purified by different methods. The chief object, however, was to prove that the peroxide is adsorbed in the surface of the platinum, the process following the usual isothermal equation $\frac{x}{M} = \alpha C^n$ where α and n are constants, M the

*Loc. cit. p. 1.

concentration of the platinum, x the amount of peroxide adsorbed, and C the total concentration of peroxide. The adsorbed peroxide is then supposed to decompose like a first order reaction equation; that is, $\frac{dC}{dt} = K'X$ where K' is a constant, C the total concentration of the peroxide and t the time. Bredig's figures lead D. A. MacInnes* to this supposition; but, owing to a lesser degree of purification, few of the figures check with Bredig's and hence difficulties have arisen in verifying the mathematical expression of the statement.

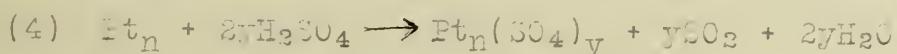
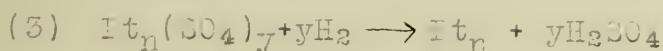
*Jour. Amer. Chem. Soc. 36, pp. 678-801. (1914).

II. Historical.

Haber* in 1898 was the first to advance the hypothesis that platinum when added to hydrogen peroxide first forms an unstable oxide, and that this oxide, in turn, reacts with peroxide yielding oxygen and water. His theory expressed by equations would be: -



Owing to the rapidity of the reaction, the unstable oxide has never been isolated. Its existence is considered much more probable since Lilbauer's** proof of the formation of $Pt_n(SO_4)_y$ as an intermediate product. He was investigating the catalytic action of platinum on the oxidation of hydrogen with sulfuric acid. For this purpose he dropped a pellet of platinum in a closed vessel containing sulfuric acid thru which hydrogen was being bubbled. He proved that the following reactions take place: -



Since $Pt_n(SO_4)_y$ is proven to exist, and since the catalytic action of platinum is similar in both cases, the formation of Pt_nO_y is made more probable.

* Ber. Anorg. Chem. 18, 40. (1898).

** Z. Physik. Chem. 17, 380. (1911).

Bredig* in 1890 studied the catalytic action of platinum on the decomposition of hydrogen peroxide. In his first publication, which came out in 1899, he agrees with Haber as to the formation of an intermediate oxide of the formula Pt_nO_y .

The evaluation of n and y were left undetermined till Grube** in 1910 proved that n is one and y is three. To accomplish this he precipitated platinum trioxide on a platinum electrode, dipped the electrode in 2N H_2SO_4 , and measured the potential. He found a steady decrease of potential from 1.517 volts to 1.046 volts. At this point it remained constant for six or eight days and then decreased to 1.020 volts. The first decrease could occur only if the platinum trioxide was dissolved in the platinum of the electrode. On measuring the potential of $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$ in 2N H_2SO_4 he found it to be 1.040 volts which agrees within .006 volts with the constant point obtained when the platinum electrode, on which PtO_3 had been previously precipitated, was dipped in 2N H_2SO_4 . This is sufficient evidence to prove that an electrode of platinum trioxide loses oxygen and in doing so follows the equation: -



Below 1.046 volts, however, a platinum electrode in which platinum trioxide is dissolved cannot give off oxygen

* S. Physik. Chem. 31, 258. (1899).

** S. Elektrochem. 16, 64. (1910).

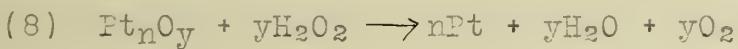
to the atmosphere. Since the potential, nevertheless, continues to decrease, Grube assumed that the PtO_y reacts with the platinum of the electrode according to the equation: -



Both reactions, (5) and (6), are reversible and hence when the velocity of formation and decomposition are equal, equilibrium exists and the potential ceases to fall. The final constant potential of 1.020 volts represents equilibrium conditions.

Therefore, according to Grube when oxygen is given off from a platinum electrode, platinum trioxide was previously formed. The intermediate product of Pt_nO_y which Haber assumed to be formed must then be PtO_3 .

As stated on page 5, Bredig accepted the equations originally set forth by Haber, that is: -



He based his experimental and theoretical work on equations (7) and (8) and from them studied the velocity of decomposition of hydrogen peroxide when catalyzed by platinum. He investigated the reaction both with pure hydrogen peroxide and with "poisoned" peroxide. A small amount of "poison" produced an unexpected change in the velocity of the catalyzed decomposition. Among the "poisons" used by him were hydrocyanic acid, iodine, bromine, carbon monoxide, oxalic acid, formic acid, phosphorus, phosphoric acid, phosphine, arsine, arsenious

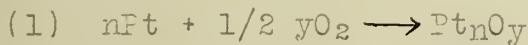
acid, hydroxylamine, hydroxylaminchlorhydrat, nitrobenzene, amylnitrite, sodium nitrite, hydrazine, pyrogallol, potassium chlorate, sodium sulfite, hydrofluoric acid, mercuric chloride, mercuric cyanide, hydrochloric acid, ammonium chloride, and sodium thiosulfate.

On measuring the velocity of decomposition of pure hydrogen peroxide, he found that the reaction corresponded roughly to a first order reaction. He computed from his data, for successive intervals of time, first order reaction constants. The values obtained instead of being constant showed a decided increase. Only a very small amount of any of the above mentioned "poisons" was sufficient to entirely change the velocity; the results of the computations of the first order constants did not, as in the preceeding case, remain constant, but showed a decided decrease.

In the present research no "poisons" were added, but the hydrogen peroxide was not purified as highly as was that which Bredig used.

III. Theoretical.

Since the formation of the unstable oxide $Pt_{n}O_y$ has been shown to be quite probable and since n and y have been evaluated as 1 and 3, respectively, $Pt_{n}O_y$ is undoubtedly formed as an intermediate product during the decomposition of hydrogen peroxide by platinum. The two steps of the process accordingly would be: -



If the reaction represented by (1) is more rapid than (2), the decomposition would be of the first order; on the other hand, if (2) is more rapid than (1), the reaction would be of the y th order. Since y has already been shown to be equal to 3 the reaction could not possibly be of a higher order than the third. Calculations of the first, second, and third order reaction constants show that the reaction is not second or third. Neither are values of the first order constants equal for successive intervals of time. If a solution of pure hydrogen peroxide in conductivity water is used, the constants calculated for successive intervals of time increase; a very little "poison", however, causes a decrease.

First order reaction constants are calculated from the equation

$$(3) \ .4543 K_1 = 1/t \log_{10} a/a-x$$

where a is the initial concentration of the peroxide, that is

when the time is zero, and $(a-x)$ is the concentration at the time t . Both a and $(a-x)$ may be expressed in arbitrary units, for eg. the volume of potassium permanganate required by 1 gram of the reacting mixture. Bredig made his calculations on the amount of permanganate required for 2 cc. of the reacting solutions.

The rapidity of a second order reaction is represented by the equation

$$(4) \frac{dx}{dt} = K_2 (a-x) (b-x),$$

where t is the time, a and b the respective initial concentrations, and x the change in concentration at the time t . In this case, however, a and b are equal. Equation (4) may then be written

$$(5) \frac{dx}{dt} = K_2 (a-x)^2.$$

Integrating both members of equation (5) and evaluating the constant gives

$$(6) K_2 = (1/t) \frac{x}{(a-x)a}.$$

The rapidity of a third order reaction is given by the equation

$$(7) \frac{dx}{dt} = K_3 (a-x) (b-x) (c-x).$$

But, when a , b , and c , are equal, as they would be if this were a third order reaction, this equation becomes

$$(8) \frac{dx}{dt} = K_3 (a-x)^3.$$

Integrating and evaluating the constant gives

$$(9) \quad K_3 = \frac{2x}{ta^2(a-x)} .$$

Below figures are given to prove that the reaction is not second or third order and that determinations of the first order reaction constants show a decrease. In the following K_1 is a first order constant; K_2 , a second order; and K_3 , a third order constant.

t	(a-x) per gram	.4343 K_1	K_2	K_3
0	16.97987			
3	12.7196	.0414	.00657	.000774
6	10.0041	.0383	.00684	.000806
9	7.9079	.0368	.00810	.000884
12	6.3305	.0357	.00825	.000972

On page 21 a run is given in which the constants increase. Bredig and Ikeda* show that this increase is not due to a slow saturation of the platinum with oxygen by using the same platinum solution in two series of runs. Their constants increase in the second series just as in the first.

One object of this research was to prove that, as D. L. MacInnes** suggests the reaction takes place by adsorption of the hydrogen peroxide on the surface of the platinum

* Loc. cit. p. 1.

** Loc. cit. p. 3.

according to the isothermal equation

$$(10) \quad x/m = \alpha (c-x)^n,$$

α and n being constants, m the platinum concentration, c the total hydrogen peroxide concentration, and x the amount of hydrogen peroxide adsorbed. When the platinum is very dilute, the amount of hydrogen peroxide adsorbed need not be used where it occurs in $(c-x)$. Equation (10) then becomes

$$(11) \quad x/m = \alpha (c)^n \quad \text{or,} \quad x = m \alpha (c)^n.$$

Substituting this in a first order equation, $\frac{dc}{dt} = K' c$ gives

$$(12) \quad \frac{dc}{dt} = K'm \alpha (c)^n.$$

Integrating between the time limits zero and t , equation (12) becomes

$$(13) \quad C_0^{(1-n)} - C_t^{(1-n)} = Kmt.$$

C_0 and C_t are the initial concentration, and the concentration at the time t , respectively, of the hydrogen peroxide. When $n = 0.8$ the equation becomes

$$(14) \quad C_0^{1.2} - C_t^{1.2} = Kmt.$$

If the equation follows the isothermal equation expressed in (11), the amount of hydrogen peroxide adsorbed will depend on the surface of the platinum exposed to it. This surface in turn, depends on the concentration and the degree of dispersion of the platinum. In a series of reactions

K_m would be a constant only for a given platinum concentration.

If values of K_m are calculated for different series of runs in which the same sample of colloidal platinum at the concentrations m_a , m_b , etc., was made, the following equation would hold

$$(15) \quad \frac{K_m b}{K_m a} = \frac{m_b}{m_a} .$$

IV. Experimental.

To determine the velocity of decomposition of hydrogen peroxide after treatment with colloidal platinum, a flask partly filled with colloidal platinum and another containing a known volume of hydrogen peroxide were placed in a thermostat at 25°C. When the contents of both flasks had come to the temperature of the thermostat, a known volume of colloidal platinum was added to the peroxide and the two solutions thoroughly mixed. By different methods a sample was taken out at known time intervals, placed in sulfuric acid so as to stop all reaction between the platinum and peroxide, and titrated with a standard solution of potassium permanganate in order to determine the amount of peroxide remaining. The concentration of the peroxide when the time is zero may be represented by a , and when the time is t by $(a-x)$. This gives sufficient data for calculating the first order reaction constant K_1 from the equation

$$.4343 K_1 = 1/t \log_{10} \frac{a}{a-x} .$$

Different methods were used in withdrawing samples.

Freig took out 2 cc. in a pipette at definite intervals of time. Because of bubbles the volume of the portions could not be measured accurately. Hence, the samples in this research were weighed by placing them in sample tubes containing sulfuric acid 9.4 N, the combined weight of tube and sample being known. The tubes were then reweighed and the amount of peroxide remaining determined by titration.

Two methods of withdrawing samples were tried. First one end of a bent glass tube was placed in the stopper of the reacting mixture, the other end in the stopper of the weighed sample tube with sulfuric acid. The latter stopper was two-holed and bore a glass rod connected with a safety flask; the second opening of the safety flask had a second glass rod, by sucking on which any amount of the reacting mixture could be drawn into the sulfuric acid. 1.5 to 3.0 grams of the sample were usually taken. Withdrawing samples by this method gave sharp decreases on evaluating the first order reaction constants. This was largely due to foreign matter in the bent glass tube. After rinsing it with distilled and conductivity water it had to be dried. If compressed air was passed thru calcium chloride, and then thru the tube, small particles of calcium chloride were carried into the tube and "poisoned" the peroxide even more so than it already was because of insufficient purification. Ether was also tried but enough remained to produce a harmful effect. The following results show that calcium chloride was less harmful than ether, and leads one to suspect that in general organic compounds are more poisonous than inorganic.

t	$.4343 K_1$	Differences	t	$.4343 K_1$	Differences
		per minute			per minute
0			0		
5	.2173	.0210	7	.0278	.00081
10	.1122	.0074	13	.0229	.00013
14	.0834		18	.0221	.00004
			23	.0219	
					Calcium Chloride
					Ether

The smaller decrease towards the end of the run is due to the fact that more of the "poison" in the tube is washed out as the run progresses.

The second method of taking out samples differed from the preceding merely in using a pipette instead of the bent glass tube. No safety flask was required and hence the operation was simplified. The pipette was rinsed with conductivity water before removing the first sample; each time thereafter it was rinsed with a small portion of the reacting mixture and this portion discarded. Very little error resulted if the pipette was not dry because it contained only reacting mixture. Since the bent glass tube arrangement was not suitable for discarding portions and could not be dried, error resulted from the liquid adhering to the walls of the tube.

No results of any value could possibly be obtained unless all flasks and pipettes with which the peroxide and platinum came in contact were immaculately clean. The containers were first filled with a solution of potassium dichromate in concentrated sulfuric acid; this was replaced successively by several portions each of tap water, distilled water, and conductivity water. The flasks in which the peroxide and platinum were kept were both previously steamed for half an hour.

In order to analyze the samples which were withdrawn at various times, a standardized potassium permanganate solution was prepared. An approximately .2 N solution was made by adding 6.3 grams of potassium permanganate to one liter of distilled water. This was standardized with sodium oxalate. .15 to .25

gram of the latter were dissolved in 200 cc. of water at 70° C., 2 cc. of concentrated sulfuric acid added, and the solution titrated with the potassium permanganate prepared as above stated. In analyzing the peroxide, a much more dilute solution than .2 N must be used so as to lower the percentage of error in determining the volume of potassium permanganate required; in the present research .02 N was taken, this being obtained by diluting one volume of the standardized .2 N with nine volumes of water.

All reaction in the mixture of colloidal platinum and peroxide is stopped when dropped in sulfuric acid. One volume of concentrated sulfuric acid was added to three volumes of water and 2 cc. of the mixture used. Since concentrated sulfuric acid is approximately 55.6 N, the acid used being three-fourths water was about 9.4 N.

The colloidal platinum was prepared by bringing two platinum wires in contact under conductivity water. These wires were connected thru a large resistance to a 110 volt, direct current circuit. In order to analyze the solution, a measured volume was evaporated to dryness in a weighed crucible. The concentration used here varied from .000580 to .000184 gram-equivalents per liter. It was found that colloidal platinum solution was easier to make if the water was previously heated to 75° or 80° C. Bredig*, however, says that colloidal platinum

*Loc. cit. p. 5.

should be prepared in a shallow dish surrounded by ice.

The hydrogen peroxide solution consisted of perihelral, which is 30% by weight of hydrogen peroxide, and of conductivity water. Usually .5 N to 1.0 N solution was started with. It was distilled under a pressure of 50 to 45 mm. and at a temperature of 28° to 38° C. Special care was taken to carefully clean all flasks and the condenser, and also rinse the same with conductivity water. The normality and conductance of all fractions of solutions treated as stated above were determined, an example being: -

Normality, Conductance, and Volume of Fraction

.09	2.1×10^{-5}	70 cc.	1
.1400	1.88×10^{-5}	70 cc.	2
.1732	1.36×10^{-5}	70 cc.	3
.1992	1.63×10^{-5}	70 cc.	4
.5894	1.38×10^{-5}	70 cc.	5
.0008		<u>50 cc.</u>	Residue
		400 cc.	

The remaining 100 cc. were lost by volatilization.

The normality tends to increase with each portion of the distillate till all the peroxide is over. This is naturally to be expected since peroxide boils at a much lower point than does the foreign matter present. Altho there is very little free acid there is always some, and this is the chief object of distillation. The conductance shows that the middle portion contains

only minute quantities of impurities. The higher conductance of the first portion is supposed to be due to contaminations from the glass apparatus even tho all parts of it have been carefully cleaned. The rise in conductance toward the latter part of the distillation can be accounted for in no other way than by saying that the foreign oxides present, silicon dioxide, and free acid slightly contaminate these. The residue, however, which is .0008 normal contains most of the foreign substances. The purity of peroxide distilled under these conditions is, hence, represented by a V-shaped curve, and the middle portion being the purest should be used in making the runs.

Bredig* used peroxide of .5 to .51%. In the present research no middle portions were this high, in spite of the fact that the solution started with was 1.4%. The low temperature used in distilling and the ice and salt mixture around the receiving flask were unable to prevent the volatilization of one-fifth of the water and more than two-thirds of the peroxide.

Since all the foreign materials were not removed before making the runs these "poisons" were present and had the same effect as if they had been added. As a result, determinations of the first order reaction constants showed a decrease.

In comparing the amount of decrease of constants in various runs where the conductivity of the peroxide is known, it can readily be seen that the lower the conductivity the less decrease there is among the constants. The following two ex-

*Loc. cit. p. 1.

amples are typical:

t	(a-x) per gram	.4343 K ₁ Differ- ences		(a-x) per gram	.343 K ₁ Differ- ences
0	0.5708		0	4.20786	
4	2.1018	.1641 .0009	4	2.235	.0637 .0046
8	.4754	.1632 .0013	8	1.417	.0591 .0028
12	.1461	.1619	12	.889	.0563 .0028
			16	.586	.0535
	Conductance	1.88×10^{-5}		Conductance	2.1×10^{-5}

In both these runs the same amounts of peroxide and platinum were used. This leads one to expect that if all foreign matter were removed, the constants would not only become equal, but even increase.

The more dilute the peroxide, the faster the decomposition should occur if the reaction follows the usual isotherm $x/m = \propto (c-x)^n$ as D. A. MacInnes* suggested. Or, in other words, the more platinum is present the faster the reaction should proceed. Experiments prove this in reality to be the case. In the above figures the second series shows sharper decrease than the first. The normalities of both may be easily calculated because the potassium permanganate was a standardized solution (.02044N). The second series then is $(4.20786 \times .02044)N$ or .0860N; the first, $(0.5708 \times .02044)N$ or .1956N.

*Loc. cit. p. 3.

The same conclusion follows if equal amounts of the same peroxide solution are used with different amounts of platinum. The more platinum the greater is the decrease.

t	(a-x) per gram	0.4343 K.	Difference	1 cc. of platinum by calculation was used with .0117 gram of hydrogen peroxide.
0	4.20786			
4	2.235	.0637	.0046	
8	1.417	.0591	.0028	
12	.889	.0563	.0028	
16	.586	.0555		
0	9.5708			1 cc. of platinum was found by calculation to be used with .0266 gram of hydrogen peroxide.
4	2.1018	.1641	.0009	
8	.4734	.1632	.0013	
12	.1461	.1519		

As was expected a larger amount of platinum in the first series results in greater decrease of 0.4343 K₁ in the first series.

The best results are obtained with samples of peroxide which have been freshly distilled. In one case, some peroxide was distilled the night of May 3rd. Three runs were made with the sample: the first, which was made the morning of May 4th gave values which increased; the second, made on the afternoon of May 4th, gave practically constant values; the third, made the morning of May 5th, gave values which decreased.

t	(a-x) per gram	.4343 K ₁	Differences per minute	Vol. of H ₂ O ₂	Vol. of platinum
0	17.7292			30 cc.	2 cc.
7	11.0876	.02711	.0003		
10	9.278	.02812	.0002		May 4th, A.M.
13	7.4800	.02882	.0001		
16	6.0458	.02920			
0	18.1527			30 cc.	3 cc.
3	10.2930	.0821			
6	6.6839	.0723			
9	3.9558	.0735	Constant.		May 4th, P.M.
15	1.5377	.0714			
0	16.9798			30 cc.	3 cc.
3	12.7191	.0418	.0010		
6	10.0041	.0383	.0005		May 5th, A.M.
9	7.9079	.0366	.0004		
12	6.3305	.0357			

These runs show that the peroxide absorbs some substances from the glass containers in which it was kept. The rapidity of contamination prevented two or more runs whose constants increase being made with the same peroxide solution and varying amounts of platinum. Contamination even occurred when the distillate was put in bottles which had been thoroughly steamed. The validity of the equation $\frac{(Km)_b}{(Km)_a} = \frac{(m)_b}{(m)_a}$ could not be proven unless

the peroxide solution could be kept "unpoisoned" for a period of at least twelve hours so as to make two runs with the same sample of peroxide.

The following data shows that $(Km)_a$, equation (14) page 11, is constant in a given run.

t	$(a-x)$ per gram	.4343 K	$\frac{C_0 - C_t}{t}$	$= (Km)_a$
0	17.729			
7	11.0876	.02711	$\frac{1.1770 - 1.1618}{7}$	$= .00217$
10	9.278	.02812	$\frac{1.1770 - 1.1561}{10}$	$= .00209$
13	7.4800	.02882	$\frac{1.1770 - 1.1495}{13}$	$= .00211$
16	6.046	.02920	$\frac{1.1770 - 1.1433}{16}$	$= .00210$

During the process of distillation pumice was placed in the distilling flask in order to prevent bumping and also to hasten the process. This, however, increased the conductivity of the distillate and showed that it was preferable to distil slowly rather than to hasten the process by adding any foreign substance. Two peroxide solutions of the same normality were distilled, the first with pumice, the second without. After distillation, the normality of the first solution was found to be much smaller than that of the second. This leads one to suppose that pumice, which offers a large contact surface to its surround-

ing medium, has a catalytic effect on the decomposition of the peroxide.

Attempts were made to obtain pure, that is, "unpoisoned" peroxide. This necessitated removal of all SiO_2 and other foreign oxides, $\text{Ba}(\text{OH})_2$ being used for this purpose. The excess of barium hydroxide was then converted into barium carbonate by passing in an excess of carbon dioxide generated from marble and hydrochloric acid. This excess of barium hydroxide which was added resulted in precipitating the greater part of the hydrogen peroxide as barium peroxide. For example, on treating a solution of 1.2 N hydrogen peroxide with barium hydroxide and carbon dioxide as described above, the distillate came over .047 N.

Lack of time prevented purification according to Sredig's* method. He treated crude hydrogen peroxide with just enough barium hydroxide to precipitate all foreign oxides and silica, and yet form only a faint precipitate of barium peroxide. The filtered solution was treated with a saturated solution of barium hydroxide. The hydrated barium peroxide was filtered off, washed, and added while still damp to dilute sulfuric acid (1:5) to alkaline reaction. This was acidified again with sulfuric acid and the clear filtered solution distilled under a pressure of 50 to 100 mm. and on a boiling water bath. His crude peroxide had a specific conductance of $397. \times 10^{-5}$; the purified product, $3. \times 10^{-5}$.

*Loc. cit. p. 5.

V. Conclusions.

The less "poisons" present and the better the degree of purification, the less decrease of constants occurs.

With pure peroxide $K_m t = C_0^2 - C_t^2$. It is supposed that $\frac{(K_m)_b}{(K_m)_a} = \frac{m_b}{m_a}$. To prove, this, however, all foreign

matter would have to be removed from the peroxide according to Bredig's method (see page 23) because these oxides if not removed hasten contamination. Stable pure solutions could be obtained thereby, and two runs made with the same peroxide solution before it is contaminated by the glass.

ACKNOWLEDGMENT

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